THE VAPORIZATION COEFFICIENT OF GRAPHITE

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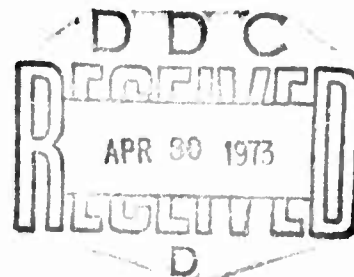
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THE VAPORIZATION COEFFICIENT OF GRAPHITE

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13. ABSTRACT Relative values of the vaporization coefficients of C, C_2 and C_3, the predominant vapor species of graphite, were evaluated by comparing the ratios between the ion intensities of different carbon vapor species obtained in a free (Langmuir) vaporization experiment and in an equilibrium (Knudsen) vaporization experiment. The measurements of the ion intensities of carbon vapor species over the spectrographic electrode grade graphite were carried out using a RF induction heating furnace coupled with a Bendix Time-of-Flight mass spectrometer The ion intensity ratio method used here is highly reliable in getting good data of relative values of the vaporization coefficients of carbon vapor species because the need of accurately knowing the temperature and also the mass spectrometer constants, ionization cross sections etc. does not arise. Both tantalum and tungsten Knudsen cells were used in the Knudsen experiments. The tantalum Knudsen cell was found to react with carbon vapor forming TaC and the TaC exchanged preferentially with C_1: the composition of the vapor was strongly affected showing a large C_3 to C_1 ratio. The tungsten Knudsen cell, on the other hand, showed no detectable evidence of reaction between the cell and the carbon vapor. By comparing the ion intensity ratios obtained in the free vaporization runs and in the Knudsen vaporization runs using tungsten cell, it was found that the vaporization coefficients of C, C_2 and C_3 over the spectrographic graphite are equal to each other within experimental scatter.
   (continued)

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The ion intensity ratio method was also applied to all the experimental data in the literature; this also showed that the vaporization coefficients of C, C_2 and C_3 over conventional graphites are equal to each other within experimental error. The most reliable value for α_1, α_2 and α_3 is 3×10^{-2} which was obtained for the condensation coefficients of C_2 and C_3 using the isotopic exchange method.

The data in literature on pyrolytic graphite was also analyzed; an interpretation of the vaporization coefficients of pyrolytic graphite is difficult as the pyrolytic graphite vaporizes predominantly from cracks, etc.

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THE VAPORIZATION COEFFICIENT OF GRAPHITE

M. HOCH AND M. YAMAWAKI

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EXPLANATION OF SYMBOLS USED IN FIGURES 6, 7, 8, 9, 10

Symbols	Experiment
○	Free Vaporization.
□	Equilibrium (K-cell) Vaporization.
◺	Equilibrium (K-cell) Vaporization. Ta in cell or lid.
◇	Ta K-cell Vaporization, this research.

Symbols	Researchers	Kind of Graphite	Type of Cell	Hole Diameter
1	Wachi and Gilmartin[6]	c-face of PG UT-6	Free	-
2	Drowart et al[5]	Finely granulated graphite	Ta or W cell with graphite liner	h/s < 10^{-5}
3	Chupka and Inghram[12]	Acheson Graphite	Ta cell with graphite liner	0.040"
4	Steele and Bourgelas[1]	RG-504	Graphite cell with Ta cap	0.025"
5	Present Work	Spectrographic graphite	W-cell Ta-cell (only for ◇)	0.04" 0.02"
6	Zavitsanos[8]	Pyrolytic graphite	Free	
6P	Zavitsanos[7]	Pyrolytic graphite	PG K-cell	0.03"
6T	Zavitsanos[7]	Pyrolytic graphite	TaC K-cell	0.03"
7	Wachi and Gilmartin[23]	Spectrographic grade	Ta cell	0.04"

INTRODUCTION

The vaporization of graphite has been studied by a number of researchers[1-7] and shown to be a quite complicated process. Carbon vapor over graphite is composed of several polyatomic species, such as C_2, C_3, C_4, and C_5, as well as atomic C.[5,6,8]

The vaporization coefficient of graphite has been determined by comparing the free evaporation rate and the effusion rate from a Knudsen cell. The experimental values reported varied between 0.001 and 0.4.

Recently, Ramakrishnan and Hoch[9] determined the condensation coefficients of C_2 and C_3 using the isotopic exchange technique and a Bendix Time-of-Flight mass spectrometer. The isotopic exchange technique used by them involved heating two powder compacts of $C^{12}(s)$ and $C^{13}(s)$ to 2663°K in a tungsten Knudsen cell. [C(s) means C atoms in the solid state.] Initially, the vaporization of $C^{12}(s)$ and $C^{13}(s)$ will produce $C^{12}(g)$, $C^{13}(g)$, $C_2^{12}(g)$, $C_2^{13}(g)$, $C_3^{12}(g)$ and $C_3^{13}(g)$ as the predominant vapor species. [C(g), $C_2(g)$ and $C_3(g)$ mean monatomic, diatomic and triatomic carbon vapor species in the gas phase, respectively.] Exchange reactions between the gaseous species and the solid generated isotopically mixed molecules $C^{12}C^{13}(g)$, $C_2^{12}C^{13}(g)$ and $C^{12}C_2^{13}(g)$ in the vapor. The exchange reactions were

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studied by analyzing the vapor effusing from the Knudsen cell using a Bendix Time-of-Flight mass spectrometer. The condensation coefficient β_2 of C_2 was evaluated from the steady state concentration of $C^{12}C^{13}(g)$. The condensation coefficient β_3 of C_3 was determined from the steady state concentration of $[C_2^{12}C^{13}(g) + C^{12}C^{13}(g)]$. The experimental values obtained at 2663°K by Ramakrishnan and Hoch were 4×10^{-2} for β_2 and 2.3×10^{-2} for β_3.

The only other experimental values of the vaporization coefficients on non-pyrolytic graphite are those given by Thorn and Winslow.[4] They estimated, from their overall vaporization data and the mass spectrometric data of Chupka and Inghram,[12] that the values of the vaporization coefficients at 2450°K were $\alpha_1 = 0.37$, $\alpha_2 = 0.34$, and $\alpha_3 = 0.08$. The values of the vaporization coefficients of pyrolytic graphite have been measured by Burns et al[10] and Zavitsansos.[8] These values, and those of Thorn and Winslow, are given in Table I. Though pyrolytic graphite is highly anisotropic, the coefficients given in Table I for the two crystal faces are quite similar because as Wachi and Gilmartin[6] noted "for the C-face, the C_2 and C_5 molecules appear to have evaporated predominantly from the edges of the ab-plane (basal plane) of the crystallites at grain boundaries, and from other discontinuities". This observation is confirmed recently by the fact that etch pits have been observed with a scanning electron microscope

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to 3000°K.[18] Other problems associated with the free
vaporization of ordinary graphites have also been described
by Wachi and Gilmartin who found that with the long
duration heating of graphite samples, the intensity of C_3,
C_2 and C_1 varies with time and that the rate of evaporation
from the surfaces increased drastically above 2900°K. Thus
it is problematical that a simple vaporization was observed.
The time dependency of the vaporization rate was explained
by Wachi and Gilmartin as follows: "in essence the continuous
transformation of closed pores to open pores and vice-versa,
the gradual attainment of steady state vapor pressure in the
open pores, the continuous changes in surface areas and
surface morphology and the continuous diminuation of C_1
and C_2 by preferential condensation and by recombination
reactions could account for the relatively large abundance
of C_3 and for the time dependency of species distribution at
constant surface temperature." The rapid increase of
total vaporization at 2900°K was ascribed by Wachi and
Gilmartin to the graphitization of the binder.

   To obtain the vaporization coefficients of the
various carbon species, it was necessary to compare rates
of effusion from a Knudsen cell, which are related to the
equilibrium vaporization rates, and vaporization rates from
free surfaces often referred to as Langmuir rates. These
two different types of measurements are generally carried
out in different laboratories and therefore direct comparison

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is quite difficult. Table II contains the heats of vaporization under Knudsen "equilibrium" conditions as given by Zavitsanos.[7] Table III, summarizing the activation energies for vaporization from free surfaces as reported by various authors, was taken from the paper by Steel and Bourgelas[11] with our addition of the uncertainties as given by Wachi and Gilmartin.[6] Since Table III shows such large standard deviations in heats for free vaporization it is meaningless to compare the data given in Tables II and III to obtain α_i. On the other hand in the work of Ramakrishnan and Hoch[9] the condensation coefficient was determined in one experiment, the errors which result from the uncertainties in the temperature of two independent determinations and the errors in the mass spectrometer constants, ionization cross sections, etc. did not arise. The aim of the present work was to confirm the fact that $\alpha_2 \simeq \alpha_3$, (as was found that $\beta_2 \simeq \beta_3$) and also to obtain a value for α_1 which could not be obtained in the isotopic exchange measurements. It must be pointed out that under equilibrium conditions $\alpha_i = \beta_i$.

The aim of the method used here again is to be able to compare vaporization rate measurements on two different species in a single experiment and thus avoid the inaccuracies of temperature measurements at high temperatures. Finally, the method developed will be applied to the experimental data of other workers, and hopefully the result will be a

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unified picture of the available data on the vaporization of graphite. This will be possible because the method developed here compares data on two different species obtained in a single experiment.

THEORY

The kinetic theory of gases gives for the rates of vaporization from a free surface:

$$m_i = \alpha_i \, P_i \left(\frac{M_i}{2\pi RT} \right)^{1/2} \tag{1}$$

where $i = 1, 2, 3, \ldots$

    m = rate of vaporization in $g \times cm^{-2} \times sec^{-1}$

    α = vaporization coefficient

    P = equilibrium vapor pressure in atm

    M = molecular weight

    T = temperature in °K.

By measuring relative ion intensities in the mass spectrometer under equilibrium (Knudsen) and free vaporization (Langmuir) conditions, I^K and I^L, respectively, ratios of vaporization coefficients can be calculated independently of any knowledge or relative ionization cross sections, multiplier efficiencies, and accurate knowledge of the temperature.

For "equilibrium" (Knudsen) conditions,

$$\frac{P_j}{P_i} = \frac{I_i^K}{I_i^K} \times \frac{\sigma_i}{\sigma_j} \times \frac{E - A_i}{E - A_j} \times \left(\frac{1 + \dfrac{h}{\alpha_j S}}{1 + \dfrac{h}{\alpha_i S}} \right) \tag{2}$$

For a non-equilibrium (Langmuir) vaporization,

$$\frac{\alpha_j P_j}{\alpha_i P_i} = \frac{I_j^L}{I_i^L} \times \frac{\sigma_i}{\sigma_j} \times \frac{(E - A_i)}{(E - A_j)} \tag{3}$$

where σ = relative cross section for ionization

E = energy of ionizing electrons

A = appearance potential

h = effusion orifice area

S = vaporizing surface area.

Combining equations (2) and (3)

$$\frac{\alpha_j}{\alpha_i} = \frac{I_j^L}{I_i^L} \times \frac{I_i^K}{I_j^K} \times \frac{\left(1 + \dfrac{h}{\alpha_i S}\right)}{\left(1 + \dfrac{h}{\alpha_j S}\right)} \tag{4}$$

In most cases $\dfrac{h}{\alpha_i S} \ll 1$, and then

$$\frac{\alpha_j}{\alpha_i} = \frac{I_j^L}{I_i^L} \times \frac{I_i^K}{I_j^K} = \frac{R_{j,i}^L}{R_{j,i}^K} \tag{5}$$

for abbreviation $R_{j,i}^L$ stands for $\dfrac{I_j^L}{I_i^L}$. Equation (5) is
the working equation of the present method. The ratio
$R_{j,i}^L$ can be determined in one experiment, and $R_{j,i}^K$ in
another. The ratios do not vary greatly with temperature;
as long as the temperature difference between the two
measurements is less than 100°, the temperature variation
can be neglected, and this method again is temperature
insensitive.

SAMPLES

The samples used were made of the ultra purity
spectrographic electrode grade graphite, grade UF4F,
supplied by Ultra Carbon Corporation, Bay City, Michigan.

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The properties of the spectrographic graphite grade
UF4F specimen are given in Table IV. Prior to measurements
the sample was outgassed by heating in the mass spectrometer
at 2050°K for 1 hour and then at 2400°K for 45 minutes.

APPARATUS

The conventional Knudsen cell electron bombardment
heating system attached to the Bendix Time-of-Flight
mass spectrometer was previously found to be inadequate
for obtaining temperatures higher than 2663°K by
Ramakrishnan and Hoch.[9] In order to get an intense
mass spectrum of carbon vapor species, temperatures
higher than 2663°K are needed. The most practical
method of attaining temperatures in the range 2200-3000°K
was assumed to be radio frequency induction heating,
even though the RF signal might interfere with the oper-
ation of the mass spectrometer.

The RF heating method in conjunction with the Bendix
Time-of-Flight mass spectrometer was tested as in an
arrangement shown in Fig. 1. The design of the induction
heating assembly was patterned after the conventional
Bendix electron bombardment Knudsen cell heating tower.
A schematic sketch of the induction heating system is
shown in Fig. 2. The assembly essentially consisted
of three parts: (1) A stainless steel base flange,
(2) a water-cooled copper work coil, and (3) a crucible

support assembly. RF power was fed into the heating coil through two high frequency feedthroughs.[22] The base plate was cooled by a separate water line which consisted of a double turn of copper tubing brazed to the bottom surface of the plate and two 1/4" diameter brass tubes brazed to the top surface of the plate at right angles to the feedthroughs. The two brass tubes supported a copper plate which was positioned above the top of the work coil. The copper plate was fitted with a removable 1 1/4" diameter copper disc containing a 3/32" diameter hole which is aligned with the slit of the ion source of the mass spectrometer. After testing several coil designs, an acceptable copper coil was made which consisted of five turns of 1/8" I.D. (3/16" O.D.) copper tubing with a 13/16" internal coil diameter. The Knudsen cell was supported by three 1/16" diameter tungsten rods spaced at 120° apart. The three tungsten rods were fixed to a tantalum stand. The entire crucible support assembly was movable. After aligning the hole of the Knudsen cell with the hole in the copper disc, the crucible support assembly was held in position by two clamps. When the hole in the Knudsen cell was lined up with the hole in the copper disc, the effusion flow from the cell could enter the ion source of the mass spectrometer.

Power for the induction heating coil was supplied by a 20 kw Thermonic radio frequency generator model 1070 which operated at a frequency of 460 kc. The efficiency

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of the heater was increased by using a variable ratio step-down transformer provided with taps for 3, 4 or 5 turns of the secondary of the transformer. The step-down transformer was a model TD-74 manufactured by Taylor-Winfield Corporation, Warren, Ohio.

Before using the induction heater in the mass spectrometer, its performance was tested in a specially constructed vacuum system. A tungsten Knudsen cell and a graphite block were heated in the vacuum system. The temperatures of the cell and the block were measured with a Leeds & Northrup disappearing filament type optical pyrometer. The pyrometer readings were corrected for the emissivity of the sample and for the glass window absorption. While the tungsten cell was heated to 2683°K without trouble, the graphite block, when continuously heated up to 2773°K, produced arcing and a glow discharge in the system. Examination of the heater after the conclusion of the run indicated a layer coating of thick carbon on the coil and the base of the feedthroughs. The high vaporization rate of graphite at 2770°K resulted in the rapid buildup of a conductive layer of carbon in the system. The carbon deposit shorted the induction coil feedthroughs to the base plate.

Since it was thought earlier that a slow pumping speed of the vacuum system can bring about arcing in the system,[9] the original vacuum system attached to the Knudsen

cell heating tower which had been supplied by Bendix
Corporation, Cincinnati Division, was replaced by a new
vacuum system, consisting of a 4" diffusion oil pump,
a 2" diameter copper tubing connecting the pump and the
heating tower and a 2" diameter vacuum valve.

EXPERIMENTAL PROCEDURE

Using RF heating and the Bendix Time-of-Flight mass
spectrometer, as previously described, the carbon vapor
over spectrographic electrode grade graphite was analyzed
both under free vaporization and equilibrium vaporization
conditions. For the free vaporization experiments,
cylindrical blocks of 1/2" diameter and 7/16" height were
cut out from a spectrographic graphite cylindrical block
of 13/16" diameter and 1 1/2" height which had been out-
gassed in an outside furnace in such a manner as described
in the section entitled SPECIMEN and used. In order to
avoid rapid buildup of a conductive layer of carbon in
the heating system, a tantalum sleeve was used in the free
vaporization experiments. The tantalum sleeve is in a
shape of cylindrical cup of 5/8" outer diameter and 5/8"
height, covering all sides of the cylindrical graphite
block specimen except the top. The top surface of the
specimen was polished with 4/0 emery paper.

In the equilibrium vaporization experiments, two
kinds of Knudsen cells were used; one made of tantalum and

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the other made of tungsten. The tantalum Knudsen cell
has an orifice of 0.040" diameter and in some runs was
provided with a graphite liner made from the same block
as the specimen itself was made from. A schematic sketch
of the tantalum Knudsen cell and the graphite liner is
shown in Fig. 3. The tungsten Knudsen cell has an
orifice of 0.040" diameter and in some run was provided
with a tantalum insert. Another tungsten Knudsen cell
having a smaller orifice of 0.026" diameter was also
used in some runs. A schematic sketch of the tungsten
Knudsen cell and the tantalum insert is shown in Fig. 3
in the report by Ramakrishnan and Hoch.[9] In general,
the orifice area to total sample area ratio, h/S, was
always less than 10^{-3}.

The temperature was measured by sighting into the
orifice of the cell with a calibrated Leeds & Northrup
disappearing filament type optical pyrometer. Corrections
due to prism and glass window absorption were made as
described previously.[9]

RESULTS

Ionization efficiency runs were made using a tantalum
crucible containing small chunks of spectrographic
graphite. The effective relative ion intensities at
2620°K for the three predominant species (C_1, C_2, C_3)
were obtained by subtracting the heights of the ion peaks

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at mass numbers 12, 24 and 36 recorded with the shutter in closed position, from the corresponding peak heights recorded with the shutter in open position, respectively. Each intensity datum is the average of at least four readings. The ionization efficiency curves as a function of bombarding electron energy, for C^+, C_2^+ and C_3^+ are shown in Fig. 4. The ion efficiency curve for Ar^+ was also obtained from the ion intensity measurement as a function of bombarding electron energy at room temperature and is shown in Fig. 4. It is apparent that at electron energies up to 20 volts no significant amount of fragmentation takes place.

In both the free vaporization and the Knudsen cell vaporization runs, relative ion intensities were measured using an electron energy of 20 volts with the shutter in the open and the closed positions, and in the temperature range 2300°-2800°K. When the shutter was closed during the measurement, at an electron energy of 20 eV, the peak heights diminished to zero except for the mass 36. The height of the mass 36 peak diminished by over 96% when the shutter was closed. The measured effective relative ion intensities, I_{12}, I_{24}, and I_{36}, and the calculated ion intensity ratios, I_{36}/I_{24}, I_{36}/I_{12} and I_{24}/I_{12}, are summarized in Table V. Each relative ion intensity value is the average of at least five readings. The standard deviation of each effective

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relative ion intensity value and the maximum error range
of each ion intensity ratio value are also given in
Table V. It should be noted that among the peak heights,
I_{12}, I_{24} and I_{36} of C, C_2 and C_3, I_{36} is generally the
largest and I_{24} is the smallest with the exception of the
results of Runs 6 and 7 in which the tantalum Knudsen
cells were used. In Runs 6 and 7, the I_{12} peak was the
smallest, (not counting I_{48} and I_{60}) while the peak
I_{36} was still the largest.

The peak heights of the carbon vapor species
heavier than C_3 were not usually large enough to allow
for their measurement except in Run 7. In Run 7, ion
peaks of C_4 and C_5 were high enough to allow the
measurements of their heights. In Table V the measured
effective relative ion intensities, I_{48} and I_{60}, and the
calculated ion intensity ratios, I_{48}/I_{12} and I_{60}/I_{12}, are
given.

After each vaporization run, the crucible and the
specimen were visually inspected. The tantalum Knudsen
cell was found to have reacted with the carbon vapor
resulting in color change of the inner wall and the
orifice wall of the cell from metallic to golden yellow.
This color change of the cell was attributed to the
formation of a TaC layer on the tantalum. Aside from
the coating of yellow color, the central ciruclar part
of the flat internal surface of the top and the corresponding

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part of the bottom of the cell were found to be covered by a thick gray fragile layer. These layers were determined to consist of carbon by means of powder x-ray diffraction. In Fig. 5, a macrophotograph of the tantalum Knudsen cell heated with the graphite liner fitted inside is shown. The central part of the inside surface of the top of the cell is seen to be of dull gray color in Fig. 5. This part is covered by a deposited carbon layer. Such a carbon layer was easily peeled off by a strong blast of air. The fragments which are seen between the top and the bottom in Fig. 5 are part of the layer which was peeled off in such a way from the central part of the inside surface of the bottom. Under the deposited carbon layer, a yellow TaC layer was again found to be present. After the conclusion of the run in which the graphite liner was used, the outer surface of the side of the liner was found to have recessed markedly; and had become much rougher than the inner surface of the liner or the surfaces of the graphite chunks inside the liner. This is indicative of the fact that marked vaporization occurred from the outer surface of the side of the graphite liner. On the other hand, no evidence of recognizable amount of reaction between the tungsten cell and carbon vapors was observed.

Combining the free vaporization and the equilibrium vaporization data, ratios of the vaporization coefficients

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of the carbon species on spectrographic graphite were calculated. In the calculation, the average of the results of Runs 1 and 2 and the average of the results of Runs 3 and 4 were used. The data obtained using the tantalum cells were omitted in the calcualtion because of the reaction of the cells with carbon vapors. Based on the data obtained from Runs 1 to 4, we get α_2/α_1 = 0.98 and α_3/α_1 = 1.52, in the temperature range from 2350° to 2800°K, for the vaporization coefficient ratios of the spectrographic graphite. This can be identically rewritten as follows: The vaporization coefficients of the three predominant carbon vapor species, C, C_2 and C_3 over the spectrographic graphite are equal to each other within a factor of two. In the DISCUSSION section, the ratios of vaporization coefficient will be evaluated in detail using all available date in the literature.

DISCUSSION

The important considerations of the results presented in Table V are that the free vaporization data seem to be consistent. The Knudsen vaporization data using the tungsten Knudsen cell and Ta insert are identical. However, the data using tantalum Knudsen cells, with and without graphite liners, show that the ratios increase which in turn seem to indicate that C_1 reacts with tantalum and also tantalum carbide preferentially. C_2 also reacts

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whereas C_3 appears to be completely inert. The sig-
nificance of this observation is the following: Most
people either use tantalum or tantalum carbide Knudsen
cells, and therefore the ratios calculated later will
have to be evaluated with this in mind. Therefore note
that not every experimentalist using a very similar
arrangement would obtain equivalent reaction. If one
uses a tantalum Knudsen cell in which there is a large
amount of graphite surface, a large effusion hole, and
the collimating system into the mass spectrometer is
sufficiently good so that only gas from the Knudsen cell
itself enters the ionization chamber (and not gas
molecules which hit the orifice or channel walls), then
the intensity ratio $\frac{I_n}{I_1}$ would not be influenced. If,
however, one uses a tantalum cell with a small orifice,
or an inefficient collimating system (as we have been
using) to collect all the vapor (including that which
strikes the orifice walls), then the ratio of the
intensities, $\frac{I_n}{I_1}$, is going to be falsified in a fashion that
would make it seem to be much larger than if tantalum
would not be present. The use of a tantalum carbide
Knudsen cell does not change the effect. C_1 reacts
with the tantalum carbide while C_3 either does not or
only does so to a much lesser extent. Therefore
even on completely carburized TaC, C_1 condenses and some
C vaporizes, probably forming equilibrium ratios of

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C_1 and C_3. Thus $\frac{I_3}{I_1}$ will be higher even if there is no net carbon gain by the TaC. This happened in Run #7 where the $\frac{I_3}{I_1}$ ratio did not change with time even though the tantalum had long been carburized to yellow TaC. The intensity of the C_2 peak can similarly be explained.

In order to use equation (5) to evaluate the ratios of the vaproization coefficients, all available data in the literature were scrutinized. Most people, when they show their data, plot the log IT (the mass spectrometry intensity multiplied by the temperature) versus $\frac{1}{T}$. From those graphs we have read off the intensities and calculated the ratios at $\frac{1}{T}$ = 3.6, 3.8, 4.0, 4.2 x 10^{-4} and so on, and obtained the ratios shown in Table VI. In cases where the experimental data had to be linearly extrapolated, the ratios are in parentheses.

Since only Steele and Bourgelas have carried out both Knudsen and Langmuir measurements, a comparison of the ratios of $\frac{\alpha_n}{\alpha_1}$ from their data and our data is given in Table VII. Table VII also contains the values of $\frac{\beta_3}{\beta_2}$ determined earlier.[9]

As expected, the data of Steele and Bourgelas and ours agree well, especially if one takes into account that Steele and Bourgelas used a tantalum cap during their measurements. If the C_1 from the Knudsen cell reacts with the tantalum cap and thus lowers the C_1 equilibrium pressure, then one will obtain a higher

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value of a_1 than should be expected under normal conditions. This would lower the values $\frac{a_n}{a_1}$ if, as we discussed before, C_n reacts less with the tantalum than does C_1. Within experimental error, Steele and Bourgelas and our data agree indicating that $a_2 = a_1 = a_3$. One has to remember here that we are using intensity ratios and that a factor of 3 in the ratio amounts to a difference in the heats of vaporization at 3000°K of ±7 kilocalories. If the factor of 3 arises from errors in all four intensity measurements, each measurement may just be off 30% to account for it; deviation in the normal log IT versus $\frac{1}{T}$ presentation will not be observable.

Other investigators' data who have used either the Knudsen or Langmuir technique are plotted in Figs. 6 and 7 from Table VI, which contains the intensity ratios, $R_{j,i}$ versus $\frac{1}{T}$. On the top of the figures we have plotted the results obtained by us using tantalum Knudsen cells, to show that some of the Knudsen data (where Ta or TaC was present) changes with temperature similarly to ours. The reason for this is at high temperature C_1 reacts more giving a higher $R_{3,1}^K$ ratio. Even if one uses a tungsten Knudsen cell for equilibrium measurements, one is not sure that no reaction will occur between carbon and the tungsten. If again, one assumes that the reactivity of C_1 is highest with the tungsten Knudsen cell, then comparison of free vaporization and equilibrium

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vaporization can only be made insofar as to say that if $R_{n,1}^{L}$ is equal to or smaller than $R_{n,1}^{K}$ then probably the measurements are correct. Looking first at Fig. 6, one sees that the data of Steele and Bourgelas,[11] both Knudsen and free vaporization ratios, vary with temperature and they move in parallel. However our data and Wachi's[6] data seem to fall on a horizontal line and our Knudsen measurements and the Knudsen measurements of Chupka and Inghram also seem to be temperature independent. If one draws a line in this Figure for $R_{2,1}$ at .45 to .5, independent of temperature; this line would represent within the experimental scatter both the Knudsen and Langmuir data, taking into account the use of tantalum Knudsen cells and the correction to be applied to those.

The situation in the case of $R_{3,1}$ is not so simple, all data seem to vary with temperature. However, looking on at our data, taken with a tantalum crucible, one also sees a large temperature dependence. At low temperature the reactivity of C_1 with tantalum is small. With this fact in mind, if one uses the Knudsen data at low temperature of Drowart et al[5] and Chupka and Inghram[12] ($\frac{1}{T} \geq 4.4$), the free vaporization data of Wachi, and the present Knudsen and Langmuir measurements, one can draw a horizontal line for $R_{3,1}$ at 4.5; which is again independent of whether it is a Knudsen or Langmuir measurement.

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This evaluation indicates that the vaporization coefficients are equal, $\alpha_1 = \alpha_2 = \alpha_3$, as was indicated earlier in Table VII. This result of the evaluation is thought to be highly reliable, because the ion intensity ratio method used here does not require an accurate knowledge of the temperature or of the mass spectrometer constants, ionization cross sections, etc. Thus, it is concluded that the vaporization coefficients of C, C_2 and C_3 over conventional graphites are all equal to 3×10^{-2}, which was obtained for the condensation coefficients of C_2 and C_3 earlier[9] using the isotopic exchange method.

Several authors determined the vaporization coefficient of pyrolytic graphite. Table I contains the data and graphite descriptions from Burns[10] and Zavitsanos.[8] The data of Burns[10] cannot be analyzed further, as they only gave the vaporization coefficient parallel and perpendicular to the C face, from which we cannot calculate the ratio of the peak intensities. On Figures 8 and 9, $R_{2,1}$ and $R_{3,1}$ intensity ratios are plotted both for free vaporization and also for the Knudsen vaporization. The lines marked in each Figure are the equilibrium Knudsen ratios derived earlier using non-pyrolytic graphites. One can see that the data of Zavitsanos[7] using pyrolytic graphite and TaC Knudsen cells, seem to scatter around this "equilibrium line". There is a temperature dependence of Zavitsanos[7] equilibrium data. The ratio increases

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when the temperature increases. A similar increase but of a larger magnitude can be seen in the free vaporization measurements of Zavitsanos[8] and of Wachi and Gilmartin.[6]

The Knudsen measurements, using pyrolytic graphite and ordinary graphite must show the same intensity ratios, and temperature dependence. If they do not, then, probably the pyrolytic graphite, is not undergoing equilibrium vaporization in the Knudsen cell. We have to assume that the variation in the Knudsen data of Zavitsanos' pyrolytic graphite measurements[6] is just scatter and the horizontal lines in both Figures 8 and 9 represent the equilibrium ratios. Comparing now the free vaporization ratios for pyrolytic graphite one notices that the $R_{2,1}^{L}$ ratio increases with temperature but its value is about that for ordinary graphites; the $R_{3,1}^{L}$ ratio also increases with temperature, but its value is much smaller than that for ordinary graphites. Thus, in the free vaporization of pyrolytic graphite we find that the $R_{2,1}$ ratio is higher than the one in Knudsen measurements and also higher than in the free vaporization measurements of ordinary graphite, whereas the $R_{3,1}$ ratio is lower than the one in the ordinary graphite and also lower than in the equilibrium measurements. If one plots the $R_{3,2}^{L}$ ratio for free vaporization, Fig. 10, one finds that this ratio is independent of temperature. Thus, the temperature dependence in the $R_{2,1}^{L}$ and $R_{3,1}^{L}$ ratios must be due to some reactivity of C_1 with the pyrolytic graphite surface, whose net effect seems to be the same as when we have reactivity with tantalum carbide.

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From the ratios of free vaporization, one has
to conclude that from a pyrolytic graphite surface, C_2
comes out easiest, i.e. its vaporization coefficient is
closer to unity. C_1 comes out less readily and C_3 comes
out with the lowest vaporization coefficient. However,
this statement would only be valid if all the species
would come off from the surface. As Wachi and Gilmartin[6]
already noted this is not the case. Thus, it is not
really possible to talk about vaporization coefficients
for pyrolytic graphite.

FUTURE WORK

The vaporization characteristics of different grades
of graphite which are commercially available will be
studied using the triple Knudsen cell and RF induction
heating tower coupled with a Bendix Time-of-Flight mass
spectrometer. The triple Knudsen cell technique was
developed by Hackworth[16] for the determination of thermo-
dynamic activity of alloys. The alloy for which one
component's activity is to be measured is placed in one
of two effusion chambers of the triple cell and the pure
isotopic standard in the other. The atomic or molecular
beams from each chamber effuse into a third chamber and
through a collimating hole into the ion source of the
mass spectrometer. The recorded intensities are pro-
portional to the vapor pressures within the chambers.

A simple calculation based upon the ratio of intensities gives a direct determination of the activity of the component of alloy. In this investigation the isotopic standard will be C^{13}. Samples of the various grades of graphite, in turn, will be placed in one of the chambers while the C^{13} standard sample is placed in the other. The vapor pressures of the carbon vapor species will be proportional to the ion signals corresponding to the C^{12}, C_2^{12}, and C_3^{12} from the normal graphite and C^{13}, C_2^{13}, and C_3^{13} from the enriched sample.

TABLE I

VAPORIZATION COEFFICIENTS OF CARBON VAPOR SPECIES OVER GRAPHITE AND THEIR RATIOS

Researchers	Type of Graphite	Electron Energy, eV	Temperature °K	Vaporization Coefficients and Their Ratios				
				a_1	a_2	a_3	a_2/a_1	a_3/a_1
Thorn & Winslow[4]	Reactor Grade	--	2450	0.37	0.34	0.08	0.92	0.22
Burns et al[10]	Pyrolytic, a-face	15,17, 20	2500	0.23	0.38	0.04	1.7	0.17
	Pyrolytic, c-face	15,17, 20	2500	0.14	0.26	0.03	1.8	0.21
Zavitsanos[8]	Pyrolytic, c-face	20	2618 ~ 2760	0.24	0.50	0.023	2.1	0.096

TABLE II

"EQUILIBRIUM" HEATS OF VAPORIZATION (kcal/mole) AT 298°K FOR C_n

Species	Zavitsanos[8] 3rd Law	Zavitsanos[7] 2nd Law	Zavitsanos[7] 3rd Law	Drowart et al[5] 2nd Law	Drowart et al[5] 3rd Law	Modified* Drowart et al 3rd Law	"Approximately-Best" Values By Palmer and Shelef[19]
C	173.5±1	170.3±1.1					170.89
C_2	202.0±1.1	209.1±1.1 206.7±1.3	203.5±1.2	197.8±1.7	200.0±1.7	197±2	199.0
C_3	188.8±1	194.5±1.2 (196.7±1)** (192.8±1.5)***	187.2±1.5 (201.9±1.5)**	188.2±1.5	189.6±2.3	185.6±2.5	193.5**
C_4		241.5 257[a]		231.3±7.1	242.3±5.8	234.8±8	257.8[a]

Free Energy functions from the JANAF Tables (unless stated)

*Using modified ionization cross sections[19] (same as in Zavitsanos' work)

**Using free energy functions by Strauss[20]

***Using free energy functions by Altman (private communication to Zavitsanos)

[a]Used free energy function 12% higher than JANAF

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TABLE III

ACTIVATION ENERGIES OF VAPORIZATION FROM POLYCRYSTALLINE GRAPHITE SURFACES

Species	Honig[17]	Chupka and Inghram[21]	Wachi and Gilmartin[6]	Steele and Bourgelas[11]
C_1	178 ± 10	177 ± 6	179 ± 5	(170)
C_2	199 ± 20	200 ± 10	195 ± 5	189
C_3	178 ± 10	200 ± 10	197 ± 10	187
C_4	-	-	241 ± 10	234
C_5	-	-	242 ± 6	236

TABLE IV
PROPERTIES OF ULTRA PURITY SPECTROGRAPHIC ELECTRODES, GRADE UF4F[*]

Ash Content	10 ppm
Grain Size	max. 0.008"
Bulk Density	1.76
Porosity	22.7 percent
Electrical Resistivity	0.00045 ohm-in
Coefficient of Thermal Expansion	
With Grain:	2.1×10^{-6} in/in/°C
Against Grain:	3.5×10^{-6} in/in/°C
Flexural Strength	
With Grain:	4,200 psi
Against Grain:	3,100 psi
Tensile Strength, with grain	2,200 psi
Compressive Strength, with grain	8,700 psi
Oxidation Threshold	426°C

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[*] Extruded graphite.

TABLE V

RELATIVE ION INTENSITIES AND RATIOS OF CARBON VAPOR SPECIES OVER SPECTROGRAPHIC GRAPHITE UF4F

No. of Run	Experimental Condition	Temp. °K	Relative Ion Intensity (Arbitrary Unit)					Ion Intensity Ratio			
			I_{12}	I_{24}	I_{36}	I_{48}	I_{60}	I_{24}/I_{12}	I_{36}/I_{12}	I_{48}/I_{12}	I_{60}/I_{12}
1	Free vaporization	2355	45.2±1.6	28.8±1.7	330±12			0.63±0.06	7.3±0.5		
2	Free vaporization	2497	49.6±3.8	12.6±1.7	220±8			0.25±0.05	4.4±0.5		
3	Tungsten K-cell with a Small Orifice	2634	3.6±1.8	1.4±1.0	13.2±2.0			0.39±0.49	3.7±2.4		
		2675	6.4±1.3	2.7±2.7	--			0.42±0.50	--		
4	Tungsten K-cell with a Large Orifice	2792	9.3±2.2	5.2±0.7	35.4±2.3			0.56±0.22	3.8±1.2		
5	Tungsten K-cell with a Large Orifice with Tantalum Insert	2415	7.7±1.6	2.6±0.6	14.5±1.6			0.34±0.15	1.9±0.6		
6	Tantalum K-cell	2435	7.9±1.2	9.8±1.1	160±4			1.24±0.33	20.3±3.6		
		2487	13.4±1.2	32.8±2.4	513±5			2.45±0.40	38.3±3.8		
7	Tantalum K-cell with Graphite Liner	2553	1.5±1.1	6.8±0.9	288±22			4.5±3.9	192±155		
		2620	4.5±0.4	11.5±0.4	434±57			2.6±0.3	96±21		
		2692	5.6±2.6	17.0±2.3	710±30			3.0±1.8	127±64		
		2661	7.7±2.6	21±5.5	683±19	2.5±1.2	5.8±1.2	2.7±1.6	89±33	0.32±0.26	0.75±0.41
		2671	32±3.4	93±1.7	2470±59	7.0±2.7	23±3	2.9±0.4	77±10	0.22±0.11	0.72±0.17

TABLE VI

RATIOS OF ION INTENSITIES OF CARBON VAPOR SPECIES OVER CONVENTIONAL GRAPHITES TAKEN FROM THE PREVIOUS DATA IN LITERATURE

Researcher	Type of Graphite	Experimental Condition	Ion Intensity Ratio	$10^4/T(°K)$								
				3.5	3.6	3.8	4.0	4.1	4.2	4.4	4.6	4.8
Wachi and Gilmartin[6]	UT-G	Free	$R_{2,1}^L$	0.48	0.46	0.44						
			$R_{3,1}^L$	4.52	4.42	4.5						
			$R_{4,1}^L$	0.063	0.0442	0.023						
			$R_{5,1}^L$	0.0863	0.0596	0.028						
Drowart et al[5]	Finely Granulated Graphite	Ta or W K-cell (h/s < 10^{-5})	$R_{2,1}^K$				0.53			0.326		0.218
			$R_{3,1}^K$				6.71			4.88		3.91
			$R_{4,1}^K$				9.16×10^{-3}			3.28×10^{-3}		(1.15×10^{-3})
			$R_{5,1}^K$				1.88×10^{-2}			6.01×10^{-3}		(1.97×10^{-3})
Chupka and Inghram[12]	Acheson	Ta K-cell (0.040" d orifice) With Graphite Liner	$R_{2,1}^K$					0.513		0.500	0.505	
			$R_{3,1}^K$					6.85		5.41	4.63	
Steele and Bourgelas[11]	Aremco RG-504	Free	$R_{2,1}^L$		0.629	0.490			0.334			
			$R_{3,1}^L$		(2.87)	2.22			1.373			
			$R_{4,1}^L$		3.59×10^{-3} (2.40×10^{-3})				(1.090×10^{-3})			
			$R_{5,1}^L$		1.132×10^{-2} (5.58×10^{-3})				(1.349×10^{-3})			
		Graphite K-cell (0.025" d Orifice) With Ta Cap	$R_{2,1}^K$		0.492	0.363			0.220			
			$R_{3,1}^K$		9.64	7.72			5.27			
			$R_{4,1}^K$		1.24×10^{-2} 6.15×10^{-3}				(1.58×10^{-3})			
Wachi and Gilmartin[23]	ZTA	Graphite cell inside Ta cell	$R_{2,1}^K$			0.51						
			$R_{3,1}^K$			12.0						

TABLE VII

RATIOS OF RELATIVE ION INTENSITIES AND VAPORIZATION OR CONDENSATION COEFFICIENTS OF CARBON VAPOR SPECIES OVER GRAPHITE

Researcher	Type of Graphite	Temp. °K	Ion Intensity Ratio						Ratios of Vaporization or Condensation Coefficient			
			$R^K_{2,1}$	$R^K_{3,1}$	$R^K_{4,1}$	$R^L_{2,1}$	$R^L_{3,1}$	$R^L_{4,1}$	α_2/α_1	α_3/α_1	α_4/α_1	β_3/β_2
Steele and Bourgelas[11]	Aremco	2378	0.220	5.27	(1.58×10^{-3})	0.334	1.373	(1.090×10^{-3})	1.52	0.26	0.69	
		2630	0.363	7.72	6.15×10^{-3}	0.490	2.22	(2.40×10^{-3})	1.35	0.29	0.39	
	RG-504	2780	0.492	9.64	1.24×10^{-2}	0.629	(2.87)	3.59×10^{-3}	1.28	0.30	0.29	
Present Work	Spectrographic UF4F	2350 ~2800	0.45	3.8		0.44	5.8		0.98	1.52		
Ramakrishnan and Hoch[9]	Fine Graphite Powder	2663										0.58

TABLE VIII

RATIOS OF ION INTENSITIES OF CARBON VAPOR SPECIES OVER PYROLYTIC GRAPHITE TAKEN FROM THE PREVIOUS DATA IN LITERATURE

Researcher	Type of Pyrolytic Graphite and Its Manufacturer	Experimental Condition	Ion Intensity Ratio	$10^4/T(°K)$					
				3.2	3.4	3.6	3.7	3.8	4.0
Wachl and Gilmartin[6]	Continuously Nucleated Pyrolytic, High Temperature Material Co.	Free Vaporization from c-face	$R_{2,1}^L$	1.68	1.54	1.07			
			$R_{3,1}^L$	3.16	2.68	1.82			
			$R_{4,1}^L$	2.06×10^{-2}	1.60×10^{-2}	(9.8×10^{-3})			
			$R_{5,1}^L$	1.93×10^{-2}	1.74×10^{-2}	(1.21×10^{-2})			
Zavitsanos[7]	Density of the PG sample 2.2 g.cm^{-3}	PG K-cell (0.03" d Orifice)	$R_{2,1}^K$		0.648	0.422		0.288	
			$R_{3,1}^K$		5.49	4.43		3.44	
	High Temperature Materials, Inc. Lowell, Mass.	TaC K-cell (0.03" d Orifice)	$R_{2,1}^K$		0.377			0.203	(0.156)
			$R_{3,1}^K$		7.26			4.97	4.19
Zavitsanos[8]	Surface Nucleated Piece, Density 2.21 g.cm^{-3}, GE, Detroit	Free Vaporization from c-face	$R_{2,1}^L$			0.952	0.857	0.788	
			$R_{3,1}^L$			0.606	0.526	0.463	
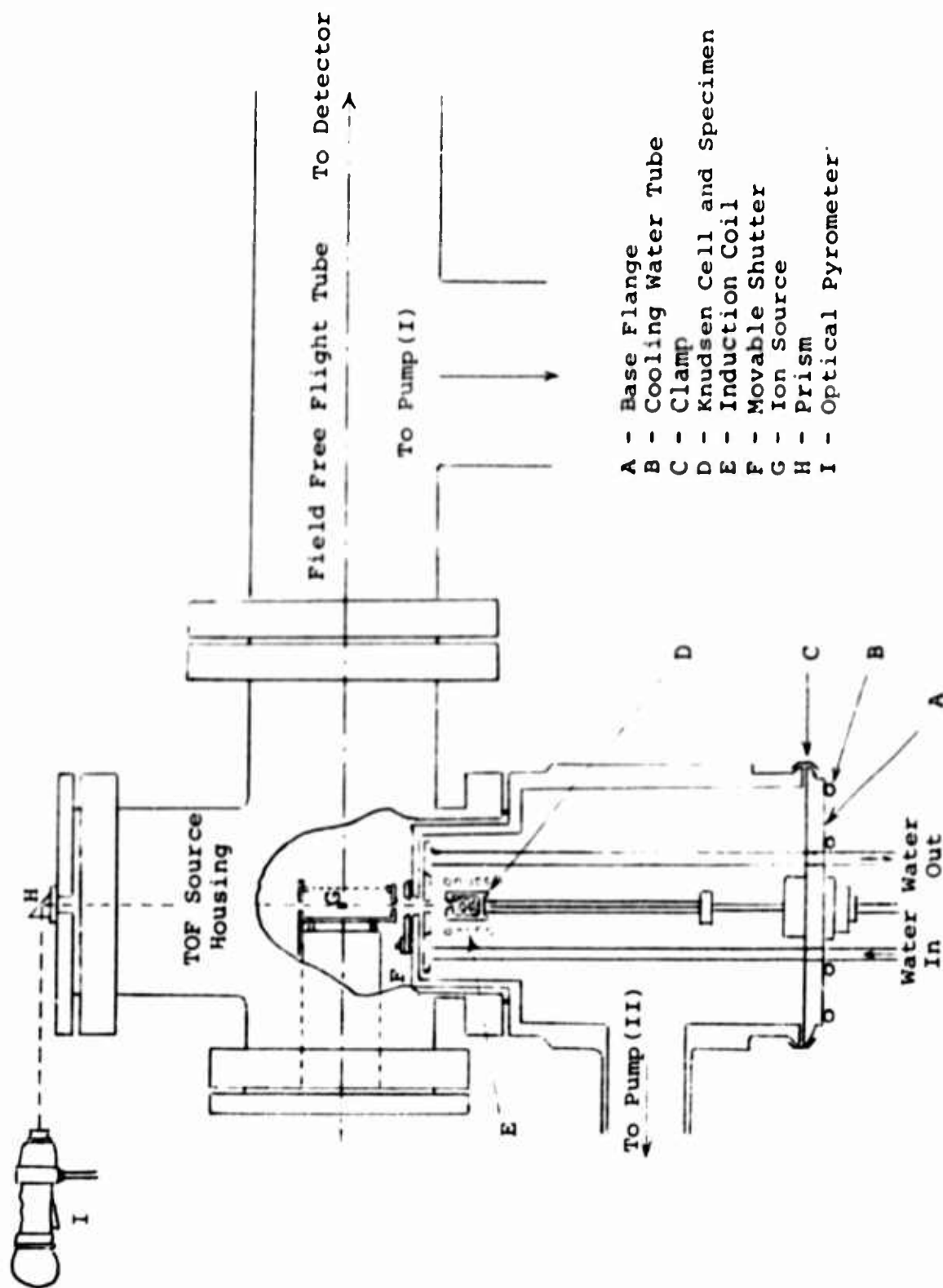
Figure 1. Knudsen Cell Induction Heater and Time-of-Flight Mass Spectrometer.

To Detector

Field Free Flight Tube

To Pump (I)

A - Base Flange
B - Cooling Water Tube
C - Clamp
D - Knudsen Cell and Specimen
E - Induction Coil
F - Movable Shutter
G - Ion Source
H - Prism
I - Optical Pyrometer

TOF Source Housing

Water Water
In   Out

To Pump (II)

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A - Induction Coil
    (H$_2$O Cooled)
B - Knudsen Cell and
    Specimen
C - Crucible Support
    Assembly
D - Base Flange
E - Copper Plate
F - High Frequency
    Feed Throughs
G - Quick Coupling Nuts
H - 1/4" Brass Tubing
I - Cooling Water Tubing

H$_2$O IN   H$_2$O IN   H$_2$O OUT   H$_2$O OUT

Figure 2.   Knudsen Cell Induction Heating Assembly.

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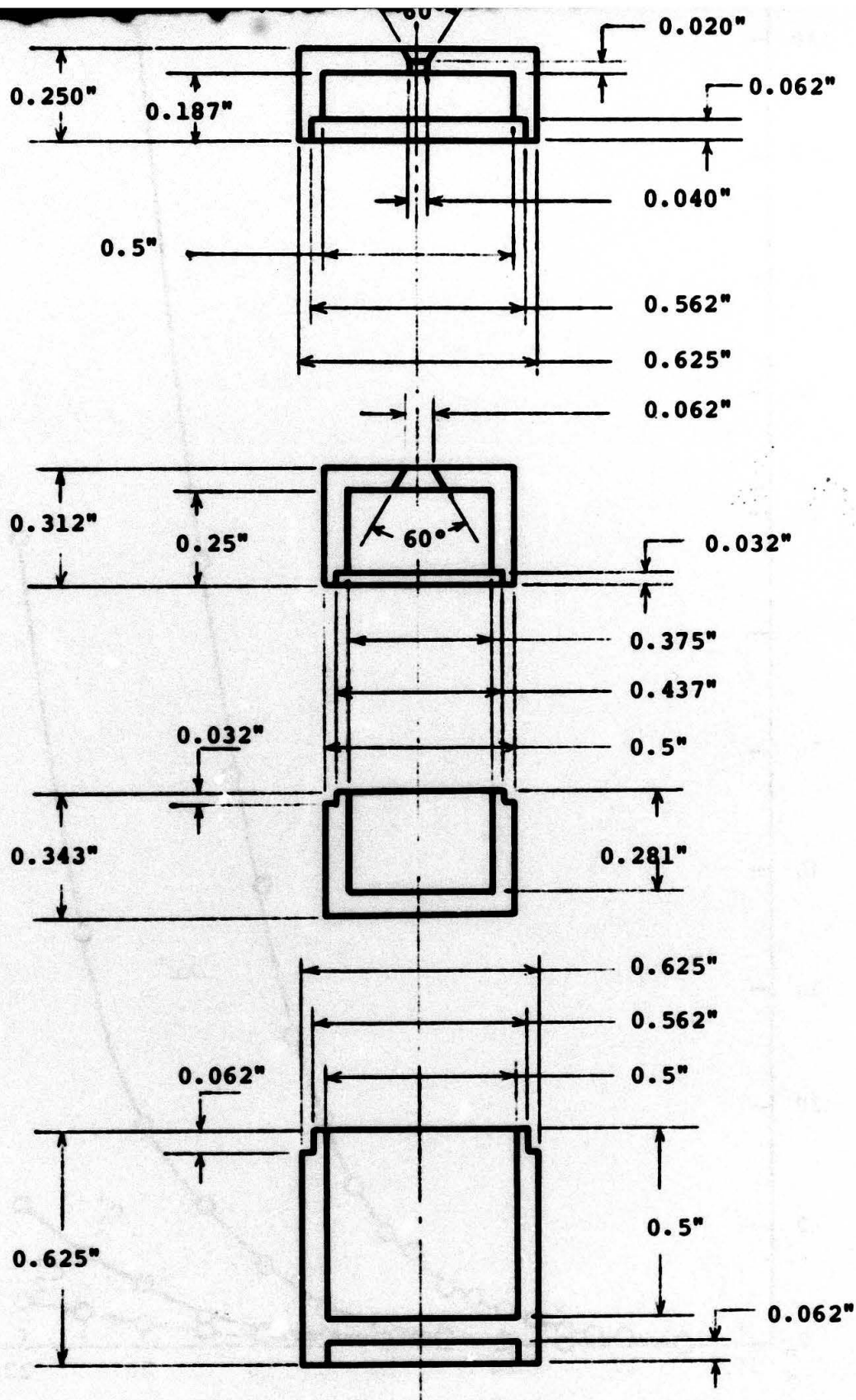
Figure 3. Tantalum Knudsen Cell and Graphite Liner.

35
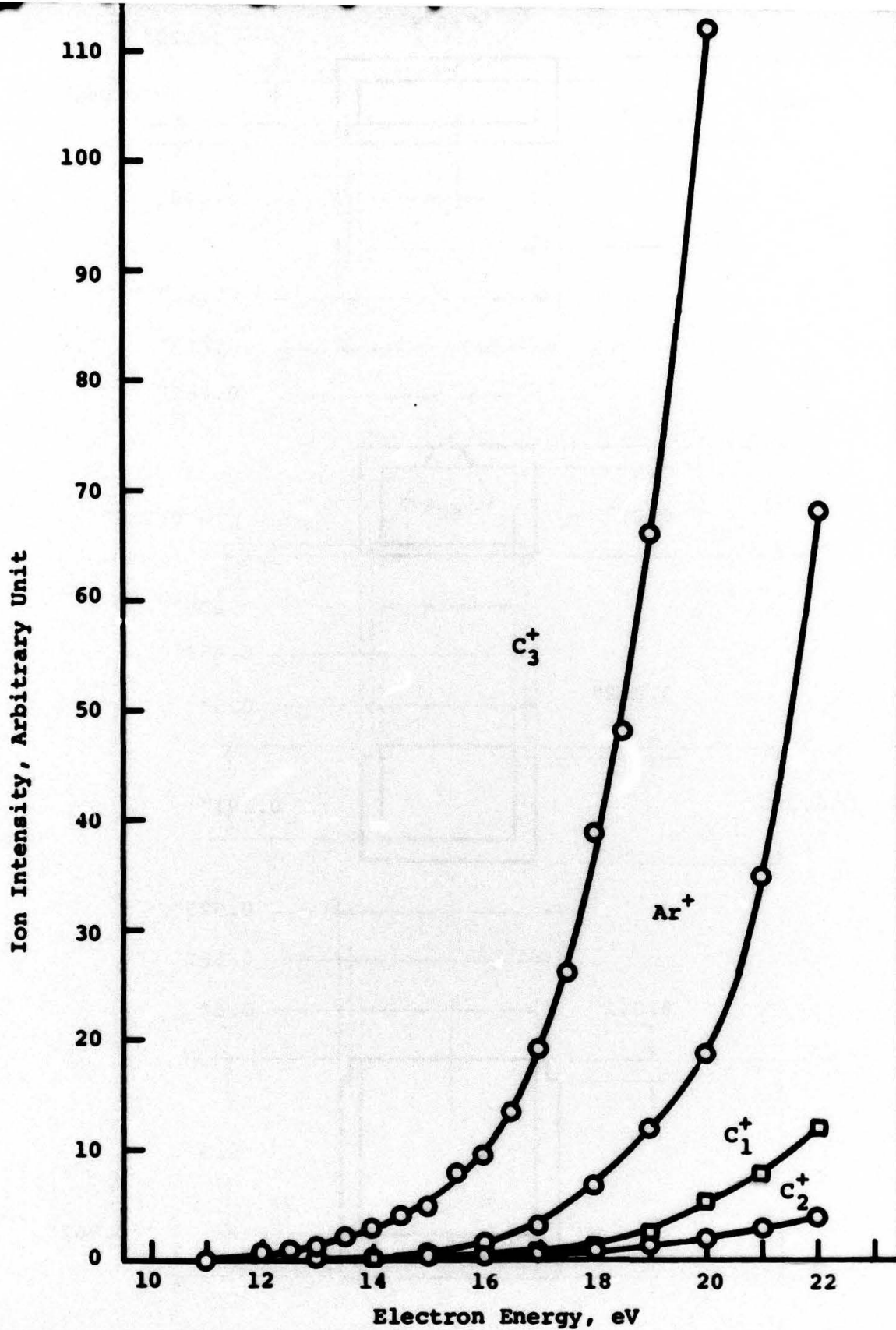
Figure 4. Ionization Efficiency Curves for Carbon Vapor Species and Argon Atom.

Figure 5.   Photograph of a Tantalum Knudsen Cell After
            Heated, With a Graphite Liner Fit Inside.
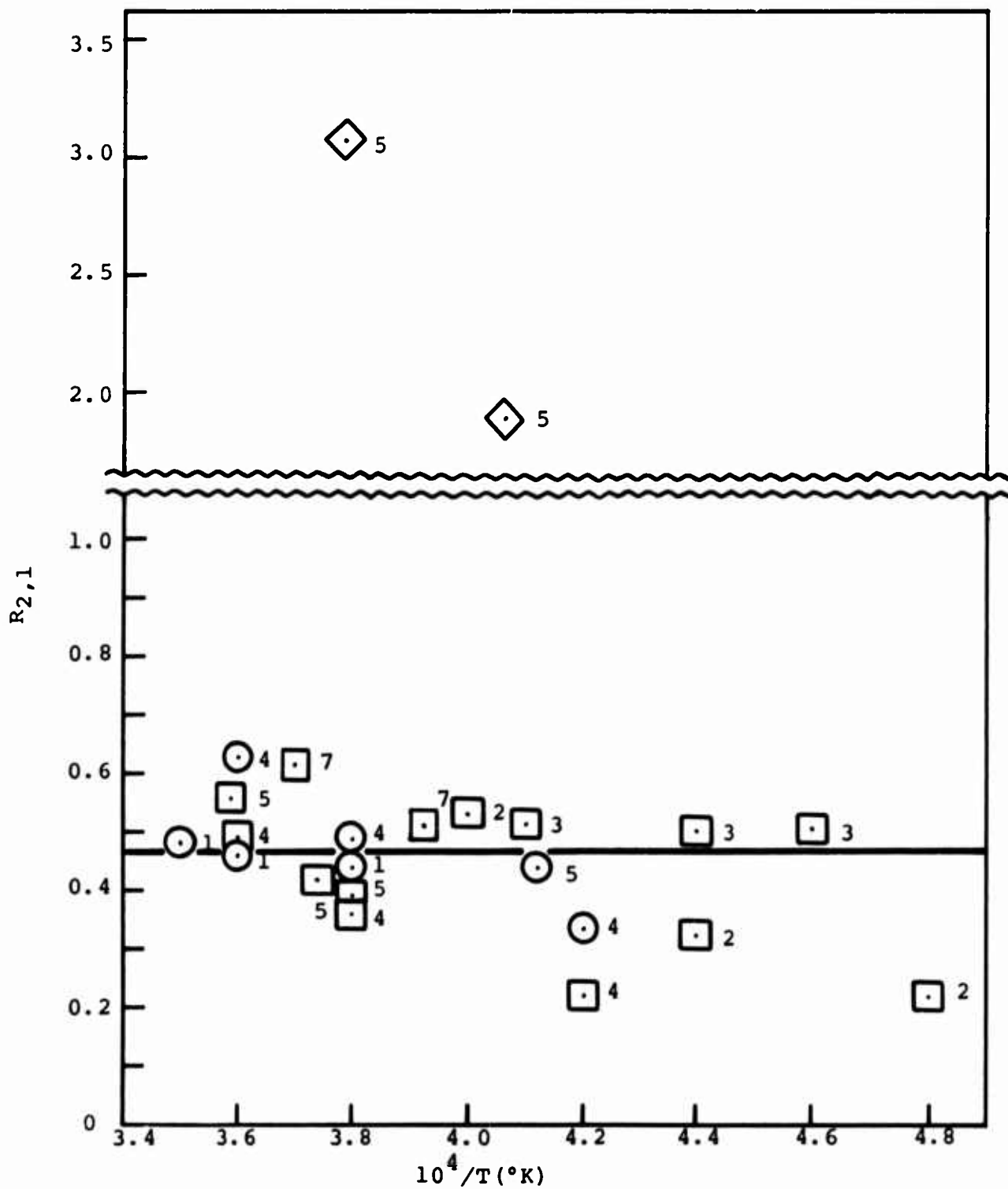   LEFT: Top of the Cell, RIGHT: Bottom of the Cell

Figure 6. Plot of $R_{2,1}^K$ and $R_{2,1}^L$ vs. $\frac{1}{T}$ for Conventional Graphites.
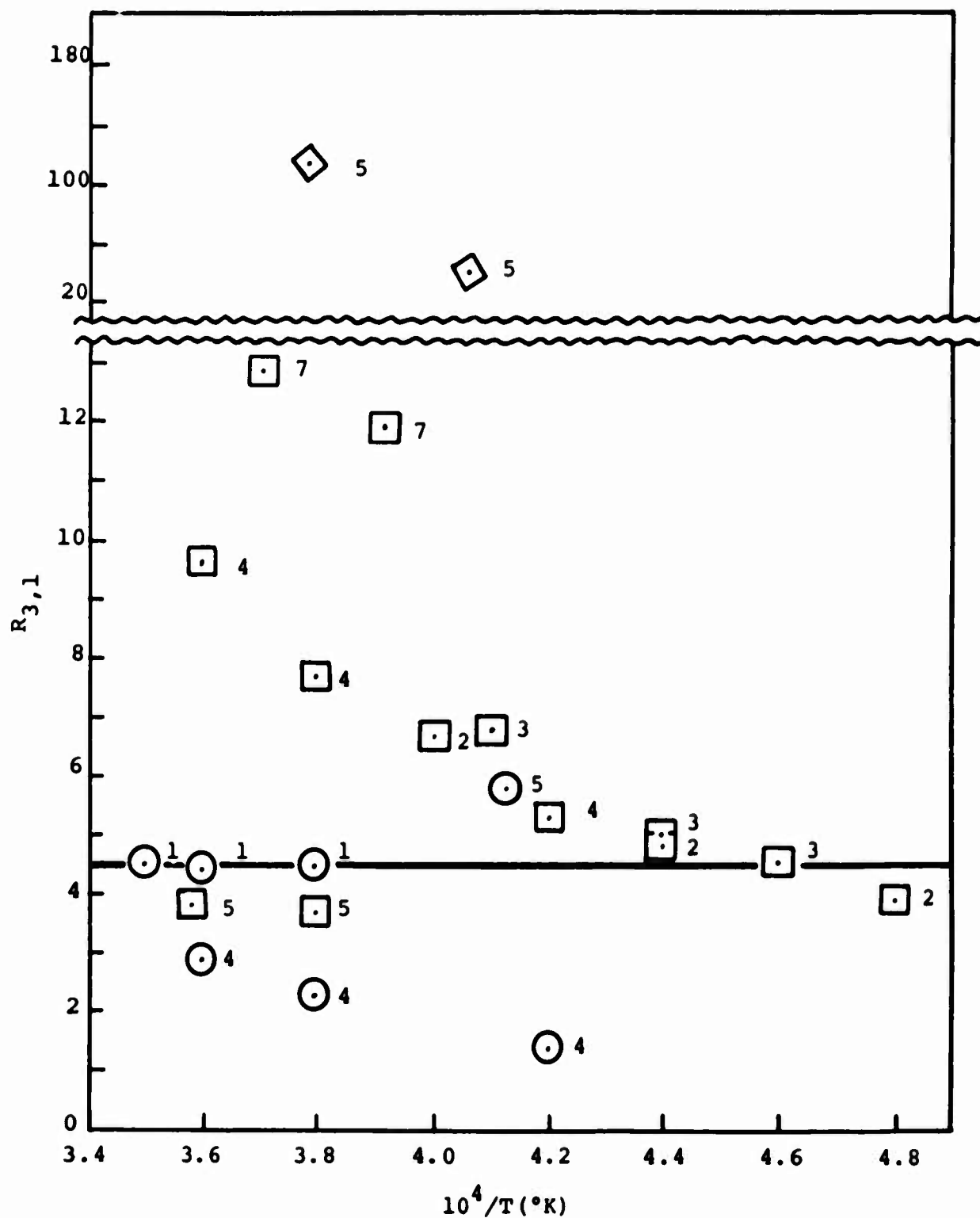
(See page viii for symbols)

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Figure 7. Plot of $R_{3,1}^K$ and $R_{3,1}^L$ vs. $\frac{1}{T}$ for Conventional Graphites.
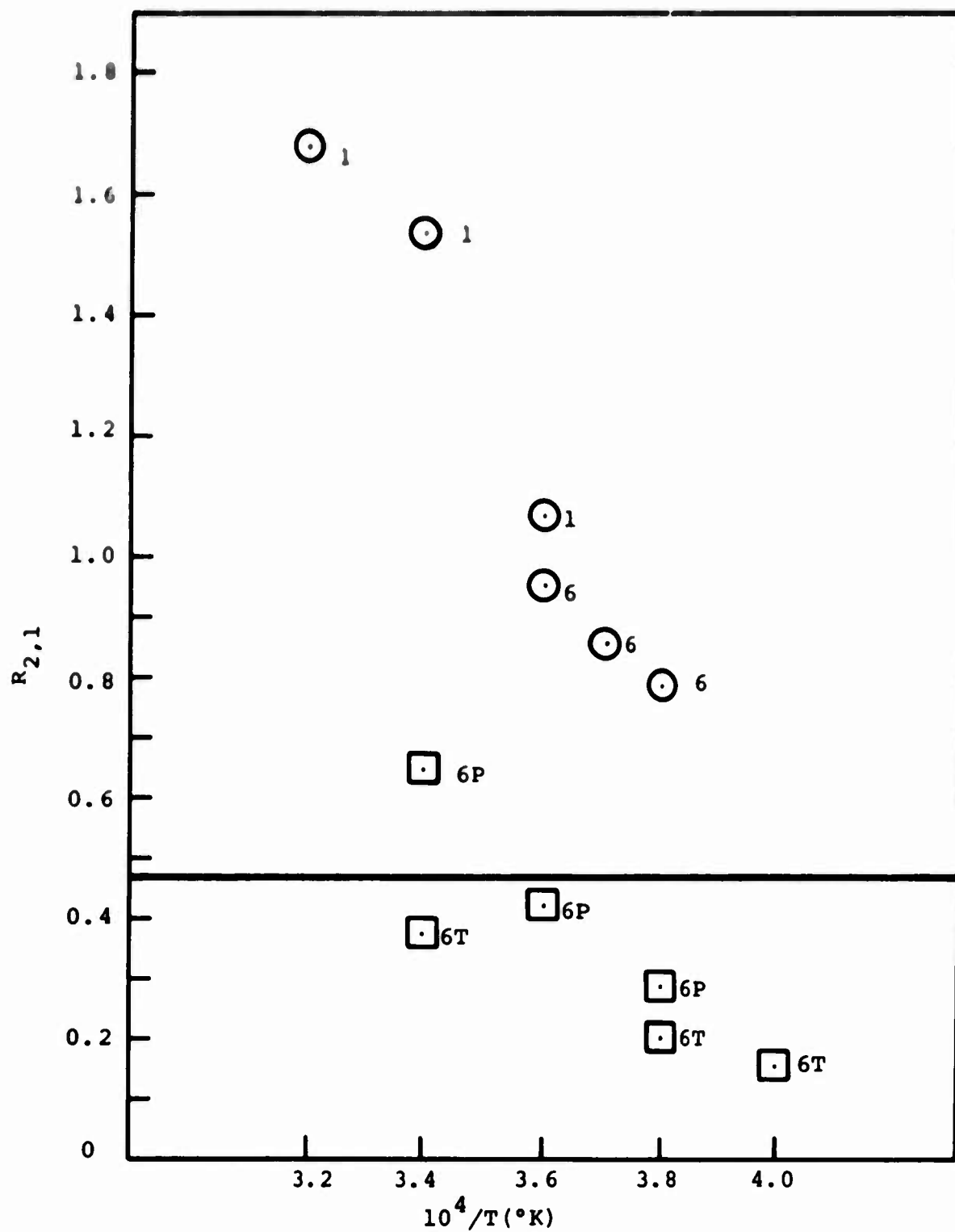(See page viii for symbols)

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Figure 8.   Plot of $R_{2,1}^K$ and $R_{2,1}^L$ vs. $\frac{1}{T}$ for Pyrolytic Graphite. (Free vaporization from c-face)
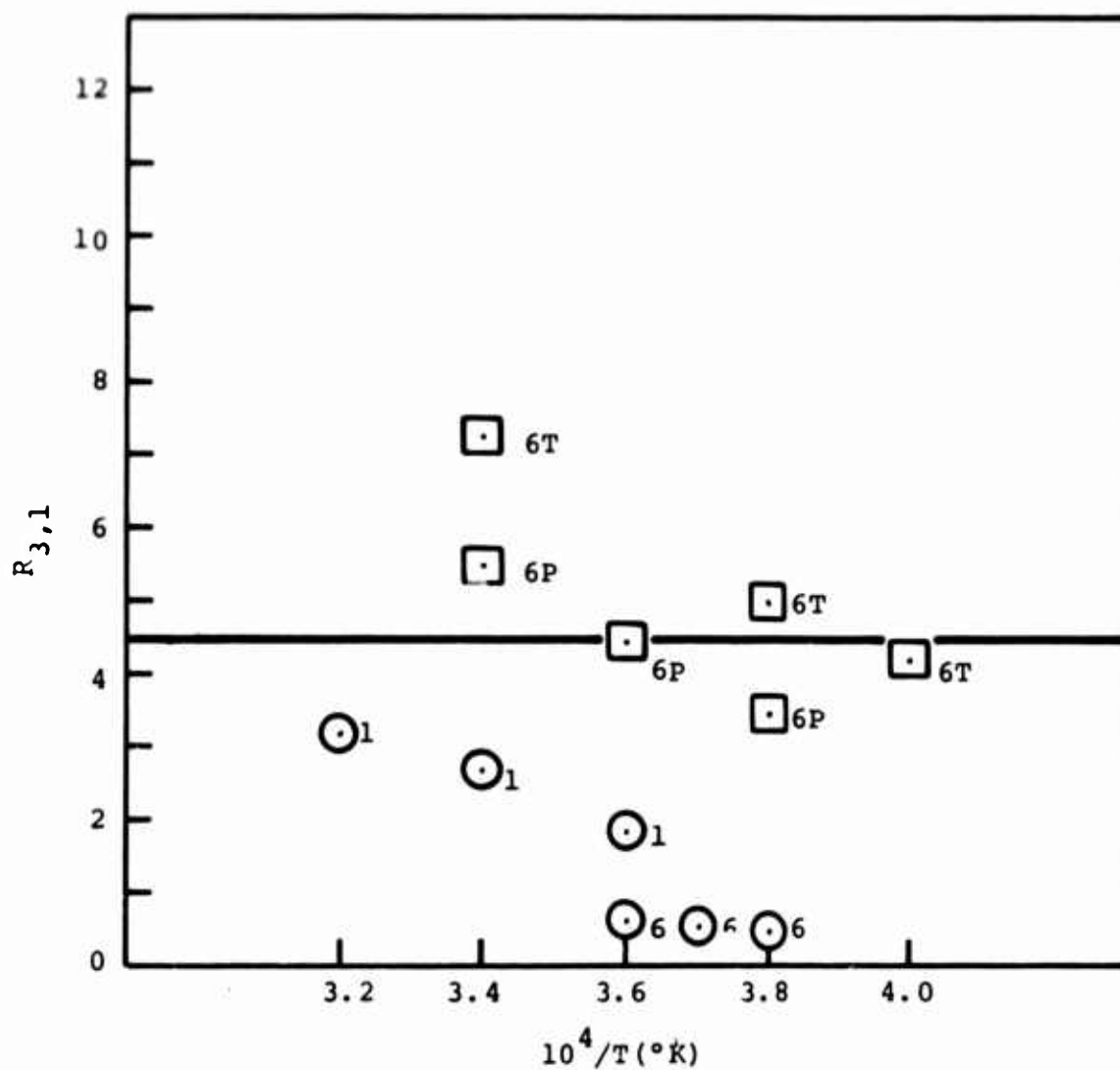
(See page viii for symbols)

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Figure 9. Plot of $R_{3,1}^{K}$ and $R_{3,1}^{L}$ vs. $\frac{1}{T}$ for Pyrolytic Graphite. (Free vaporization from c-face)

(See page viii for symbols)

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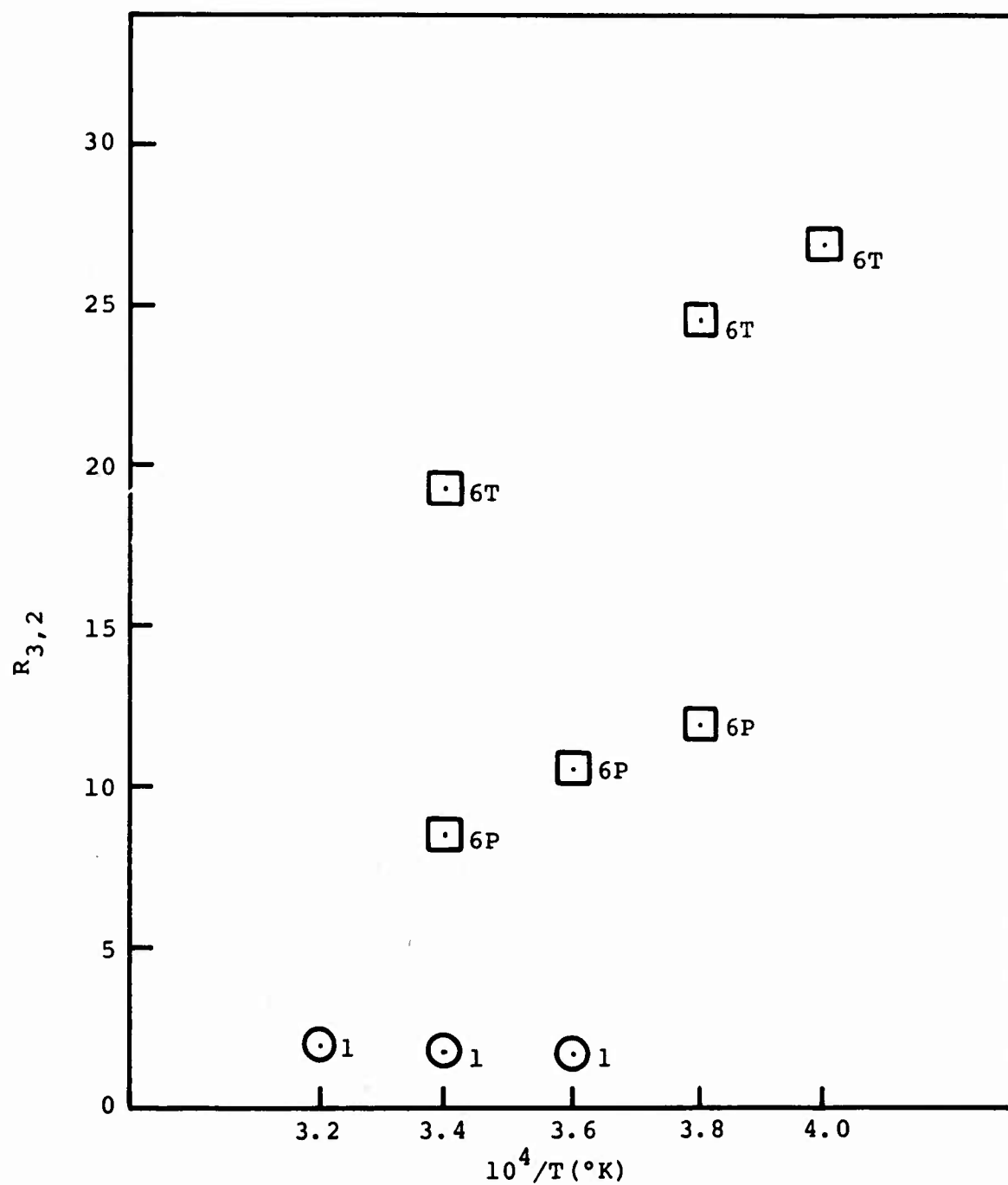Figure 10. Plot of $R^K_{3,2}$ and $R^L_{3,2}$ vs. $\frac{1}{T}$ for Pyrolytic Graphite. (Free vaporization from c-face)

(See page viii for symbols)

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